

## **PERFORMANCE OF THE ACWA PILOT SCALE IMMOBILIZED CELL BIOREACTOR IN DEGRADATION OF HD AND TETRYTOL PAYLOADS OF THE M60 CHEMICAL ROUND**

Mark A. Guelta, Nancy A. Chester, Carl W. Kurnas, Mark V. Haley  
U.S. Army Edgewood Chemical and Biological Center, APG MD 21010

F. Stephen Lupton, Mark Koch  
Honeywell International, Des Plaines IL 60017

In 1996, public laws 104-208, 105-261, and 106-79 established and expanded the Assembled Chemical Weapons Assessment (ACWA) Program. To address public concerns over the safe destruction of the U.S. chemical weapon stockpile; the ACWA program was tasked to identify two or more viable alternative technologies to the “baseline” destruction method of incineration. Neutralization followed by biodegradation was one technology identified as having potential.

Guelta and DeFrank<sup>1</sup> conducted preliminary laboratory studies using 1-liter Immobilized Cell Bioreactors (ICB) to degrade hydrolyzed agents. These studies demonstrated the effectiveness of the ICB system to degrade hydrolyzed HD agent feed. In two follow-on studies, each conducted at Edgewood Chemical and Biological Command (ECBC), Edgewood MD, a scaled-up 1000-gallon pilot ICB system was operated for three and four months respectively. Over the course of these tests the ICB system degraded 61,274 lbs of 3.8% HD hydrolysis created from the HD stockpile stored at APG. Also degraded was approximately 2320 lbs of hydrolyzed tetrytol produced at the Pantex plant, Amarillo, TX. The neutralization/biodegradation process achieved a 99.9999% overall destruction removal efficiency (DRE) for HD agent, Tetrytol and schedule-2 compounds. This paper describes the ICB system and overall process employed for the ACWA Demonstration/Engineering Design Studies.

### **INTRODUCTION**

Water Hydrolysis of Energetic and Agent Technology (WHEAT) is one alternative process to incineration proposed for complete destruction of warfare munitions containing energetics, propellants and mustard or nerve agents. The WHEAT technologies will be used to demonstrate destruction of materials representative of the M60, 105 mm projectile (HD/Tetrytol). The WHEAT technologies include water jet for cutting and boring operations to remove components from metal projectiles, a hydrolyzation step to detoxify and make biologically available projectile chemical components, and a high temperature steam process for 5X treatment of metal parts and other solid wastes. A more complete description of the entire study is available in the ACWA Demonstration Study Plan<sup>2</sup>. Viable alternatives to incineration must demonstrate a total solution to all aspects of the assembled chemical weapon destruction process.

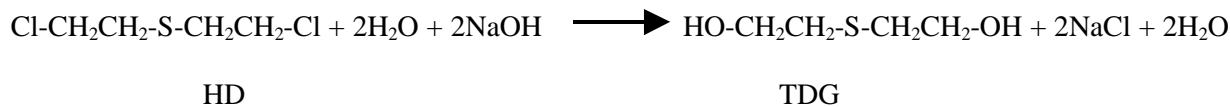
The development of the ICB pilot scale design is based on a history of past benchtop/laboratory-scale studies with hydrolyzed HD. The use of Sequencing Batch Reactors (SBR) has demonstrated the ability to successfully degrade hydrolyzed HD<sup>3</sup> and was subsequently selected as the process-of-choice

Report Documentation Page				Form Approved OMB No. 0704-0188	
Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.					
1. REPORT DATE <b>00 JAN 2002</b>		2. REPORT TYPE <b>N/A</b>		3. DATES COVERED <b>-</b>	
4. TITLE AND SUBTITLE <b>Performance Of The Acwa Pilot Scale Immobilized Cell Bioreactor In Degradation Of Hd And Tetrytol Payloads Of The M60 Chemical Round</b>				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S)				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) <b>U.S. Army Edgewood Chemical and Biological Center, APG MD 21010; Honeywell International, Des Plaines IL 60017</b>				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT <b>Approved for public release, distribution unlimited</b>					
13. SUPPLEMENTARY NOTES <b>This article is from ADA409494 Proceedings of the 2001 ECBC Scientific Conference on Chemical and Biological Defense Research, 6-8 March , Marriott's Hunt Valley Inn, Hunt Valley, MD.</b>					
14. ABSTRACT					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT <b>UU</b>	18. NUMBER OF PAGES <b>7</b>	19a. NAME OF RESPONSIBLE PERSON
a. REPORT <b>unclassified</b>	b. ABSTRACT <b>unclassified</b>	c. THIS PAGE <b>unclassified</b>			

for chemical destruction of HD in ton containers at the Edgewood Chemical Biological Center. Further research in the area of neutralization/biodegradation by Guelta and DeFrank<sup>1</sup> of ECBC, led to success in the degradation of HD hydrolysate and VX nerve agent by ICBs thereby laying the groundwork for expansion of the process to include the burster fills found in mustard agent projectiles. This report describes the demonstration run of a pilot-scale ICB system and its ability to degrade a feedstock of chemical agent (hydrolyzed HD as the sole carbon source for the microbial culture) mixed with energetic (Tetrytol) in proportions that simulate the contents of the M60 projectile.

## METHODS AND MATERIALS

HD Hydrolysate is produced by adding HD to heated water and then agitating until the HD is degraded to thiodiglycol, plus a few breakdown products. This process is described by Harvey et al.<sup>3</sup>. The primary product of the hydrolysis of HD is thiodiglycol (TDG). The NaOH required for the neutralization of the acids generated by the hydrolysis can be added either before or after the reaction. Studies have shown that a more complete conversion to TDG is achieved when the NaOH is added after the reaction has reached completion (Harvey et al.<sup>3</sup>). The reaction (without intermediates or by-products) is summarized below.



The HD hydrolysate used in these studies was prepared at an initial HD concentration of 3.8%.

In 1999 ACWA<sup>4</sup> funded demonstration testing of the ICB system as part of the larger ACWA program demonstration/validation study<sup>4</sup>. The ICB system was scaled-up to a 1000-gallon reactor housed in two 40-ft transportation containers. The HD/Tetrytol ICB system, located at ECBC, was operated by U.S. Army researchers for a 6-week validation period.

The ACWA demonstration program designated eight specific goals and objectives for the WHEAT HD biotreatment and associated systems. From the ACWA Program Study Plan, these objectives are listed below:

1. Validate the ability of the unit operation to eliminate schedule 2 compounds (TDG) present in the HD/Tetrytol hydrolysate feed.
2. Confirm the absence of HD agent in the unit operation's effluents.
3. Validate the ability of the agent hydrolysis process and the ICB, flocculation reactor, and clarifier unit operations to achieve a DRE of 99.9999% for HD.
4. Validate the ability of the energetic hydrolysis process and the ICB, flocculation reactor, and clarifier unit operations to achieve a destruction and removal efficiency (DRE) of 99.999% for Tetrytol.
5. Develop mass loading and kinetic data that can be used for scale-up of the ICB flocculation reactor, and clarifier unit operations.
6. Validate the ability of the catalytic oxidizer to eliminate chemical agents and schedule 2 compounds from the ICB process gas stream.
7. Determine the potential impact of operating conditions on the fouling and plugging of the catalytic reactor.
8. Characterize gas, liquid and solid process streams from the ICB, flocculation reactor, clarifier, and catalytic oxidizer unit operations for selected chemical constituents and physical parameters, and the presence/absence of hazardous, toxic agent and schedule 2 compounds.

The principle components of the HD/Tetrytol bioreactor system were housed in two 40-by 8-foot transportation containers (Figures 1 & 2). Major components include a 200-gallon feed tank for mixing HD and Tetrytol hydrolysates, a 200-gallon feed tank, a three-chambered 1000-gallon steel ICB tank, a 100-gallon flocculation reactor, a 300-gallon clarifier, and the water recycle system. The water recycle system consisted of activated carbon, microfiltration and reverse osmosis filter cartridges, and a 1000-gallon recycle water storage tank. A catalytic oxidation system and lime scrubber treated the air exhausted from the ICB. The pilot-scale ICB was designed to process 200 gallons of feedstock per day for a hydraulic retention time (HRT) of five days. Daily feedings of 200 gallons were to contain 40 gallons of 3.8% HD hydrolysate and 1.9 gallons of Tetrytol hydrolysate and the balance with recycled water. Sixty-five percent of the 200-gallon per day effluent was to be recycled into the system after sludge removal and desalination.

The ICB was initially filled with tap water for system checks and verification. Upon startup of the system<sup>2</sup> enough water was removed to allow addition of 55 gallons of a bacterial inoculum cultured by Honeywell<sup>5</sup>. During the run, additional sludge collected from Back River publicly owned treatment works (POTW) was added to the ICB. The system was initially started in a batch mode to allow bacterial growth and adaptation to the feed stream. The system was allowed a 32-day run-up period before starting the 40-day validation run at the required feed rate of 40 gal HD hydrolysate and 1.9 gal Tetrytol hydrolysate per day.



Figure 1. ICB, feed tank, foam knockout drum, sump drum and CATOX system in trailer one.



Figure 2. Fenton's reactor, clarifier, RO system, dirty water tank and recycle water storage tank in trailer two.

## RESULTS

The ICB HD hydrolysate produced for the ICB feed was generated at the ECBC chemical transfer facility. The principle hydrolysis/breakdown product from this procedure is thiodiglycol, which is the sole carbon source for the ICB bacteria. Forty-seven drums of HD hydrolysate were used during the demonstration test. These drums were analyzed for HD and its breakdown products. These data are summarized in Table 1.

TABLE 1. Summary of data for 3.8% HD hydrolysate.

Analyte	Mean (mg/L)	STD-D
pH	8.25	4.2
Thiodiglycol	24060	1324.6
Thiodiglycol sulfoxide	99.19	66.2
1,4-dithane	113.5	46.3
1,2-bis(2-hydroxyethylthio) ethane	586.9	296.7
(2-hydroxyethylthio) ethane thiodiglycol	286.7	178.9
1,2-bis(2-hydroxyethylthio)ethyl ether	703.9	235.2
1,4-dithane-1-(2-chloroethane)	76.79	33.84
Total Organic Carbon	10823	172.9

\*-pH in standard units (SU)

The pilot ICB feed (S1), ICB chamber 1(S3), and ICB out-fall (S5) chemical oxygen demand (COD) was measured daily as a near real-time indicator of performance (Figure 3). A COD removal efficiency

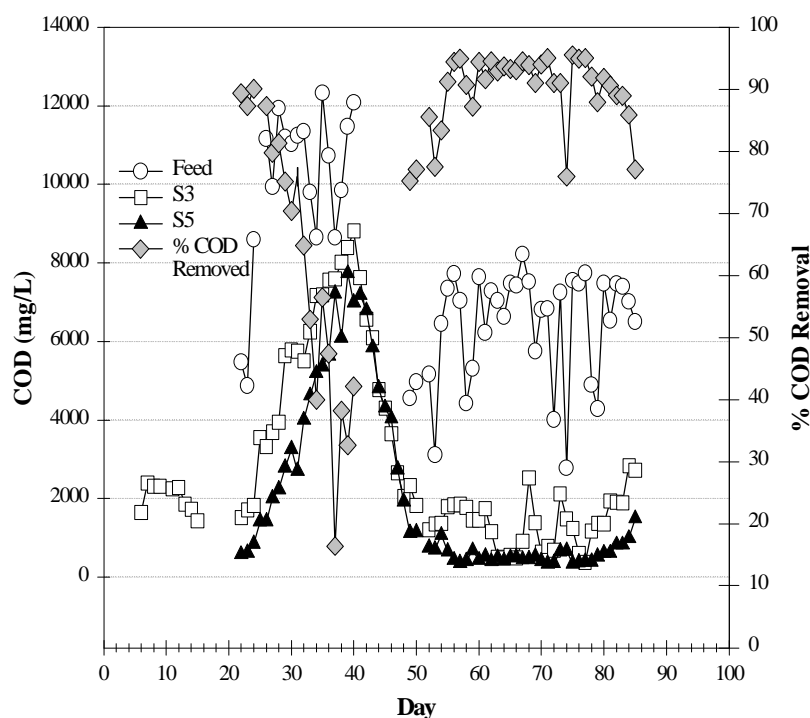


Figure 3. COD values for S1, S3, S5 and COD removal efficiency at location S5

of 90% is considered a good indicator of complete utilization of the hydrolysate as food when measured during process monitoring. However, the true performance indicator is the measure of TDG removal. The feed rate of 40 gallons/day of 3.8% HD hydrolysate was stopped on day 40 after the reactor COD levels rose and TDG was detected in the ICB out-fall. The ICB was placed in batch mode until COD levels recovered. This set back was attributed to insufficient pH control and unseasonably cold weather in the Maryland area, and in the test bay that kept the ICB temperatures between 55 and 65°F during the start-up period.

The biodegradation of TDG produces an acidic by-product. PH for this system was controlled by a single caustic addition loop. The insufficient pH control capacity kept the pH in ICB chamber 1 between 5.0-6.5 for the first 40 days of operation. These two factors slowed biomass growth and contributed to poor initial performance. To remedy this, an additional 55 gallons of municipal sludge was added to the reactor, additional pH control capacity was added with a second pH control loop, sodium bicarbonate was added to the feed, and radiant heaters were placed in trailer 1 to keep the ICB temperature above 70°F.

To speed time to validation testing, the feeding regimen was lessened to 26.6 gal/day HD hydrolysate and 1 gal/day tetrytol hydrolysate. After recovery, the ICB was placed in continuous feed mode. Reduction in COD values at the ICB out-fall were 90% or greater for the rest of the study. PH and ICB temperatures were also in acceptable ranges for the remainder of the test.

After restart of testing to include lowered feed rate, HD and HD-breakdown products were measured in the feed (S1), chamber 1 (S3) and the ICB out-fall (S5). Those data are summarized in Table 2. At no time was HD ever detected in the hydrolysate, feed, or any effluents of the ICB.

TABLE 2. Schedule-2 and Breakdown Products by Week and Sample Location

Sample Date	Analyte	S1 (mg/L)	S3 (mg/L)	S5 (mg/L)
March 24	1,4-Dithane	15.6	0.7	0.4
	Thiodiglycol	3840	825	ND
	1,4-Thioxane	24.4	4.9	3.2
March 30	1,4-Dithane	17.98	5.22	0.52
	Thiodiglycol	3510	55.4	ND
	1,4-Thioxane	13.0	4.31	3.28
April 7	1,4-Dithane	14.05	2.88	ND
	Thiodiglycol	3310	ND	ND
	1,4-Thioxane	28.5	6.52	1.15
April 14	1,4-Dithane	11.1	1.85	ND
	Thiodiglycol	3257	ND	ND
	1,4-Thioxane	1	1	ND
April 21	1,4-Dithane	8.9	9.43	9.45
	Thiodiglycol	3241	186.3	ND
	1,4-Thioxane	173.7	6.21	6.27
April 28	1,4-Dithane	10.06	9.83	5.05
	Thiodiglycol	3836	12.4	ND
	1,4-Thioxane	<1	6.96	6.11

During validation testing, air exhausted from the ICB was treated with a catalytic oxidation (CATOX) system. Exhaust gases were sampled on the same dates as liquid effluents. No HD, Tetrytol or schedule 2 compounds were detected during the test period. Exhaust gas flow rates and temperature through the CATOX was monitored daily. No plugging of the CATOX or decreases in CATOX operating temperature were observed. Daily flow through the system was 55-60 CFM; CATOX operating temperature was 775-800°F.

It is anticipated that liquid effluents may require disposal as hazardous waste. The Toxicity Characteristic Leaching Procedure (TCLP) analysis was performed on liquid effluent samples. In Maryland, any waste originating from any chemical agent is considered hazardous and must therefore be disposed of in a hazardous waste disposal facility. Generally, effluents from biodegradation

of hydrolyzed HD pass criterion established as non-hazardous waste, except for some special state codes like the Maryland code "MD-02" for waste originating from chemical agent.

The eventual site of any full-scale facility will come under scrutiny of that state's effluent discharge regulations and other requirements for an operating permit. In the event an operating permit may be required at a later date, samples of all effluents and exhaust streams were analyzed to attempt to completely characterize all outputs from the ICB system. These analyses included: Total Organic Carbon, Metals, Volatile Organic Chemicals, Semi-volatile Organic Chemicals, Cations, Dioxins, Furans, Mercury, Anions, Phosphate, Sulfate, Nitrates, Chloride, Energetics, Sulfides, Aldehydes, Ketones, Formaldehyde, Hydrogen sulfide, and Hydrogen cyanide. Waste collected in 275-gal waste tanks were analyzed using TCLP criteria. The results indicated waste generated was below Maryland state TCLP

regulatory limits. Due to the page limit of this paper, those results are not listed. These data are available from the coordinating contractor, Arthur D. Little, Inc.<sup>6</sup>, with the permission of PM ACWA<sup>4</sup>.

## CONCLUSION

The basic ability of microorganisms cultured from activated sludge to degrade HD hydrolysate under laboratory and bench scale studies were again tested in the 1000-gallon pilot scale ICB system. While laboratory and bench scale studies of this system worked well, it can't be automatically assumed that if scaled up properly any pilot-scale biological system will work as efficiently as its laboratory predecessor. While this ability has been previously demonstrated in SBRs using HD hydrolysate as feedstock, the addition of energetic materials and the proposed utility of an ICB system necessitated a demonstration study of this type.

In addition to the challenge of scaling up a biological system, what would be the effect of the energetic hydrolysate? The primary goal of the WHEAT system is to provide a total alternative solution to incineration for destroying and detoxifying the combined waste from assembled chemical weapons systems. The hydrolysis step of the WHEAT process eliminated the primary components of the energetic materials, TNT and RDX. It was expected that the energetic wouldn't undergo any further measurable degradation and would simply pass through the system. For the most part that appears to have been the case. Most of the energetics and breakdown products were below detectable limits in the feed and all effluent samples.

Based on the ACWA program's eight designated specific goals and objectives for the WHEAT and biotreatment systems, we conclude the following:

1. The hydrolysis process eliminated HD and Tetrytol in the ICB feed stream to below detectable limits.
2. Data show no HD/Tetrytol was ever detected in the ICB feed, intermediate process or effluent streams.
3. Data show that the WHEAT system and ICB successfully achieved an Destruction Removal Efficiency of 99.999% for HD.
4. Data show that the WHEAT system and ICB successfully achieved an Destruction Removal Efficiency of 99.999% for Tetrytol.
5. Mass loading data were developed for scale-up. However<sup>2</sup> additional data are required and will be developed in a follow-on engineering design study (EDS).
6. Data show that the catalytic treater allowed no release of agent or schedule 2 compounds.
7. Data show no plugging or fouling of the catalytic treater from the ICB operation.
8. Although not completely reported here, all effluents and waste streams were characterized. No hazardous or toxic agents or schedule two compounds were detected.

While the ICB validation study was successful<sup>2</sup> improvements to the system should be made, particularly within the water recycle process. The RO system seems inappropriate for the amount of salt produced by the system. Plugging of the RO membrane and filters with unsettled particulate presented an intermittent problem. Perhaps an alternative method of effluent recycling may be employed. The feed schedule did not reach the desired contribution of 40 gal/day HD hydrolysate, perhaps partially due to some less than optimum bacterial growth conditions and time constraints placed on the study.

During the summer of 2000 ACWA<sup>4</sup> funded a follow-on Engineering Design Study (EDS). Changes were made to the ICB system to address problems encountered during the demonstration study. Three control loops were installed to improve pH control in the ICB, one for each ICB chamber. To improve effluent recycle ability the RO unit was replaced with an evaporator/condenser system serviced by a 25-

ton chiller. This system produced recycle water that may have improved the ICB culture health in comparison to the water from the RO system. The HD hydrolysate feed regimen of the EDS was also increased over the 4-month test to 50-gal/200-gallons of feed/day. Feed also included water collected from the continuous steam treater (CST) testing of metal parts and dunnage decontamination. During this successful test, no schedule-2 or HD breakdown products were detected in the ICB liquid effluent or exhaust gases. Water recycle efficiency was greatly improved with liquid waste generation dropping from 1:157 (lbs HD/lbs waste) to 1:27. Parsons/Honeywell<sup>2</sup> incorporated the data collected into a 35% design package by for their total solution for the Pueblo Chemical Depot full-scale facility.

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